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Note

Selective phenylation of naphthoquinones and coumarins using diphenylmercury

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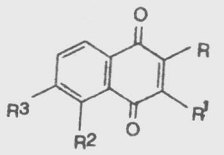
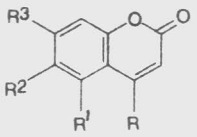
Under the influence of UV light, 1,4-naphthoquinones **1-5** and coumarins **6-10** on reaction with diphenylmercury in acetonitrile under nitrogen atmosphere give corresponding 2-phenyl- 1,4-naphthoquinones **11-15** and 4-phenylcoumarins **16-20**

Phenylquinones have been used as pigments[1] and possess biological and chemotherapeutic properties[2]. Phenylcoumarins occur in the heartwood of various timbers and some of them possess insect and termite repellent properties[3]. Phenylquinones have been prepared in the past using phenyldiazonium salts, di-*t*-butylphenol, palladium acetate, triphenyl stilbene and phenylmercuryl chloride[4] while phenylcoumarins were prepared using conventional Pechmann and Dakin condensation[5]. Diphenylmercury has been extensively used for the phenylation of various moieties, such as nitroalkanes[6], and in the synthesis of variety of compounds, like phenylketones[7].

In the present note, the use of diphenylmercury (DPM) for the phenylation of naphthoquinones **1-5** and coumarins **6-10** is reported. The reaction proceeds with a high degree of regioselectivity and provides a new route to the synthesis of phenylnapthoquinones **11-15** and phenylcoumarins **16-20** from the already existing quinonoid and coumarin nucleus. The phenylation occurs at active quinonoid position, i.e. double bond flanked by carbonyl groups on either side. In coumarins reaction occurs at C-4 position because of the more stability of free radical at benzylic position. In all reactions monophenyl products were obtained except with compound **4** where the chelation of carbonyl group by hydroxyl group enhances the electrophilic character of active quinonoid positions and as a result both mono and diphenylquinones are formed. In a typical reaction,



1	$R=R^1=R^2=R^3=H$	11	$R=C_6H_5$, $R^1=R^2=R^3=H$
2	$R=Cl$, $R^1=R^2=R^3=H$	12	$R=OH$, $R^1=C_6H_5$, $R^2=R^3=H$
3	$R=OH$, $R^1=R^2=R^3=H$	13	$R=R^1=C_6H_5$, $R^2=OH$, $R^3=H$
4	$R=R^1=R^3=H$, $R^2=OH$	14	$R=C_6H_5$, $R^1=R^3=H$, $R^2=OH$
5	$R=R^1=R^2=H$, $R^3=CH_3$	15	$R=R^2=H$, $R^1=C_6H_5$, $R^3=CH_3$



6	$R=R^1=R^2=R^3=H$	16	$R=C_6H_5$, $R^1=R^2=R^3=H$
7	$R=R^1=R^2=H$, $R^3=OH$	17	$R=C_6H_5$, $R^1=R^2=H$, $R^3=OH$
8	$R=R^2=H$, $R^1=R^3=OH$	18	$R=C_6H_5$, $R^1=R^3=OH$, $R^2=H$
9	$R=R^1=H$, $R^2=R^3=OH$	19	$R=C_6H_5$, $R^1=H$, $R^2=R^3=OH$
10	$R=R^1=R^2=H$, $R^3=OC_2H_5$	20	$R=C_6H_5$, $R^1=R^2=H$, $R^3=OC_2H_5$

when a mixture of 1,4-naphthoquinone (1 mmole) and DPM (1 mmole) dissolved in acetonitrile (65 mL) ws irradiated with UV light for 2 hr, 2-phenyl-1,4-naphthoquinone was obtained. Under similar conditions substituted 1,4-naphthoquinones **1-5** and coumarins **6-10** gave the corresponding 2-phenyl-1,4-naphthoquinones **11-15** and 4-penyl-coumarins **16-20** (see Table I).

Experimental Section

The melting points are uncorrected, IR spectra were recorded on Perkin-Elmer 599-B spectrophotometer; UV spectra on Shimadzu UV-Vis 260 spectrophotometer; ^{1}HNMR spectra in $CDCl_3$ on Perkin-Elmer R-32 spectrometer (90 MHz) using TMS as internal standard; mass spectra and elemental analysis were carried out at RSIC, Chandigarh.

Reaction of naphthoquinones 1-5/coumarins 6-10 with DPM in acetonitrile under UV light. A mixture of naphthoquinone/coumarin (1 mmole) and DPM (1 mmole) in acetonitrile (65 mL) was

Table I—Characterisation data of naphthoquinones and coumarins

Reactants	Time (hr)	Product	Yield (%)	m.p. °C	Spectral data
1	2.0	**11**	40[4]	—	—
2	2.0	**11**	70[4]	—	—
3	1.5	**12**	60	230	UV : 221, 262, 272 nm ^{1}HNMR: δ 7.3 (s, 1H, OH), 7.5-7.6(m,5H,C_3-Ph), 7.7-7.9 (m, 2H, $C_{6,7}$-H's), 8.2-8.4 (m, 2H, $C_{5,8}$-H); MS:250(M^+, 100%), 194, 165.
4	2.0	**13**	50	196	UV:232, 306, 412 nm ^{1}HNMR:δ 7.1-7.5 (s, 2H, $C_{6,7}$-H), 7.6-7.7 (m, 10H, Ar-H), 7.8-7.9 (m, 1H, C_7-H), 12.3 (s, 1H, chelated OH); MS : 326 (M^+, 100%), 298, 221, 120, 92, 77
		14	40	112	UV:229, 302, 414 nm ^{1}HNMR:δ 7.1 (s, 1H, C_2-H), 7.3-7.5 (m, 2H, $C_{6,7}$-H), 7.6-7.7 (m, 5H, C_3-Ph), 7.8 (m, 1H, C_8-H), 11.8 (s, 1H, OH) MS:250 (M^+, 100%), 222, 221, 120, 92
5	2.0	**15**	40	62	UV:254, 314 nm ^{1}HNMR:δ 2.5 (s, 3H, CH_3), 7.2-7.3 (m, 6H,C_3-Ph,C_5-H), 7.4-7.5(m,2H,$C_{7,8}$H), 7.6 (s, 1H, C_2-H), MS:248 (M^+, 100%), 220, 219, 118, 90, 76
6	8.0	**16***	60	105	UV:230, 260 nm ^{1}HNMR:δ 6.1 (s, 1H, C_3-H), 7.1-7.5 (m, 4H, Ar-H), 7.6 (s, 5H, C_4-Ph)
7	8.0	**17**	61[8]	-	-
8	8.0	**18**	50[9]	-	-
9	8.0	**19**	45[9]	-	-
10	8.0	**20***	58	135	UV:230, 258, 350 nm ^{1}HNMR:δ 1.5-1.7 (t, *J*=7.0 Hz, 3H, CH_2CH_3), 4.0-4.3 (q, *J*=7.0 Hz, 2H, OCH_2), 6.2 (s, 1H, C_3-H), 6.9-7.5 (m, 3H, Ar-H), 7.6 (s, 5H, C_4-Ph)

*Products **16** and **20** gave satisfactory C, H analysis

taken in a 100 mL quartz vessel equipped with nitrogen inlet, teflon coated opening for sample removal and a water-cooled condenser (Applied Photophysics immersion well reaction RQ 125). An immersion well-condenser in combination with a source of UV light (Applied Photophysics, medium presure UV lamp, 6 W, $\lambda > 254$ nm) was placed into the solution in which nitrogen was bubbled slowly and the reaction mixture was irradiated. After irradiation the reaction mixture was concentrated under reduced pressure on Buchi rotavapour. Residue was chromatographed on silica gel and elution with pet. ether, benzene and ethyl acetate successively, gave unreacted starting material and the corresponding products, 2-phenyl-1,4-naphthoquinones **11-15** and 4-phenylcoumarins **16-20** which were characterised by their chemical and spectral data (see Table 1).

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